

COPOLYMERIZATION REACTIONS OF CARBON DIOXIDE

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ABSTRACT

Polymerization reactions of carbon dioxide were investigated with a view toward utilization of vast amounts as a chemical feedstock. Copolymerization of carbon dioxide with formaldehyde and paraformaldehyde in the presence of a variety of catalysts was investigated. In the presence of amine catalysts or Lewis acid catalysts, carbon dioxide copolymerizes with formaldehyde or paraformaldehyde to give a water-soluble polymer of polycarbonate structure. A 1:1 alternating copolymer is proposed from its infrared spectra showing a strong ester band at 1750 cm^{-1} . From high-pressure liquid chromatography analysis, number-averaged molecular weight was determined to be about 20,000. However, mixing in 25% of a comonomer spacer (ethylene glycol) gave a polymer with twice the molecular weight. The addition of boric acid resulted in cross-linking of the polymer and a significant increase in the viscosity of the aqueous solution.

INTRODUCTION

Since 1969 when Inoue and coworkers (1, 2) first reported the synthesis of high-molecular-weight poly(propylene carbonate) by copolymerization of CO_2 and propylene oxide using organozinc catalysts, copolymerization of carbon dioxide has been widely studied (3). Because of the low cost and accessibility of the monomers and the attractive properties of polycarbonates, there has been considerable recent interest in the development of catalysts for the alternating copolymerization of carbon dioxide with epoxides (3-7). Recently, Chiang (8) reported copolymerization of carbon dioxide and formaldehyde to give a 1:1 alternating copolymer. The nature of the product from alternating copolymerization of CO_2 with carbonyl compounds in the presence of a variety of acid and base catalysts is reported here.

EXPERIMENTAL

Reactions were conducted in a 300-mL pressurized Parr autoclave with generally 16 g of CO_2 and an equimolar amount of aldehyde equivalent with 5% by weight of catalyst. Products were worked up differently depending on the solvent for the reaction. In a typical run, a mixture of aqueous formaldehyde (37%), catalyst, and dry ice was placed in a 300-mL Parr reactor. The reactor was sealed under nitrogen and heated at the desired temperature for the desired time period. The reaction products were soluble in the water solvent used for the reaction. For the reactions of paraformaldehyde and trioxane, methyl *tertiary* butyl ether (MTBE) or dioxane were used as solvents.

Polymer products were analyzed by infrared (IR) spectroscopy and gel permeation chromatography (GPC). Aqueous solutions of the polymeric products were analyzed with high-pressure GPC on a TSK30 gel column with water eluent and ultraviolet (UV) detection at 210 nm, and dioxane solutions were analyzed with a mixed pore size photoluminescence gel column in tetrahydrofuran (THF) solvent. Molecular weights (M_w) were calibrated using retention times of proteins and polymer standards with narrow M_w distributions. Reaction yields were also determined on the GPC column. The copolycarbonate peak area was calibrated using a known concentration of a standard consisting of a purified copolycarbonate sample.

RESULTS AND DISCUSSION

Base Catalysis

A comparison of the catalytic effects of a series of organic bases was conducted on the reactions of carbon dioxide with aqueous formaldehyde to form the acetal copolycarbonate ester (Figure 1). The reactions were performed in a pressurized autoclave at 120°C using organic bases, triethylamine (TEA), dimethylaminopyridine (DMAP), and diazabicyclooctane (DABCO) as catalysts for the reactions (Table 1). Chiang used TEA as the catalyst (8). The DMAP and DABCO are much more basic and were expected to exert a better catalytic effect.

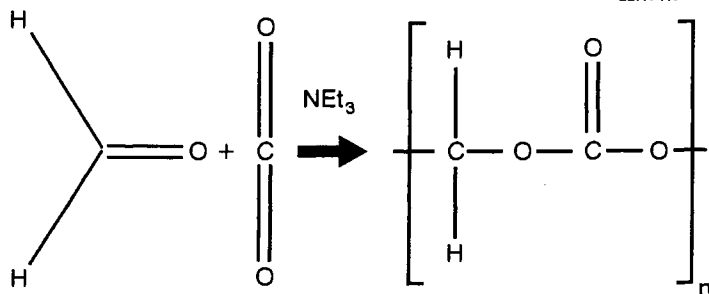


Figure 1. Acetal copolycarbonate formation.

TABLE I

| Reactions of Formaldehyde | | | | | | | |
|---------------------------|-------------------|---------|-----------|----------|------------------------------|---------------------------------|---|
| Aldehyde | Catalyst | Solvent | Temp., °C | Time, hr | Polymer | Solubility | M _w (yield) |
| HCHO (37%, 40 mL) | TEA (2 g) | Water | 120 | 100 | Very viscous oil (4.01 g) | Somewhat soluble in water | 23,000 (1%) 20,000 (17%) 16,000 (19%) 12,000 (8%) |
| HCHO (37%, 40 mL) | DMAP (2.3 g) | Water | 120 | 100 | Very viscous oil (6.2 g) | Somewhat soluble in water | 22,000 (8%) 14,000 (27%) 11,500 (15%) 1000 (20%) <1000 (rest) |
| HCHO (37%, 40 mL) | DABCO (2.24 g) | Water | 120 | 100 | Very viscous oil (5.1 g) | Somewhat soluble in water | 22,000 (22%) 1000 (17%) <1000 (rest) |

* HCHO = formaldehyde.

The product from aqueous formaldehyde reaction was water-soluble. Extraction of the product with ether recovered about 70% of the base catalyst. The amount of the acetal polycarbonate was determined by GPC. Polymer peaks eluted early, and molecular weights and amounts were determined from retention times and peak areas. Low-molecular-weight oligomers were also present in the products, as evidenced by the presence of a late GPC peak. The results in Table I show that higher yields of polymer were obtained from the reaction using the more powerful base DMAP. TEA gave the lowest yield and is the most volatile.

Water was removed from the reaction products by low-vacuum distillation. The impure reaction products were tacky solids with good water and ethanol solubility, but poor solubility in THF and dioxane. IR spectroscopy of the products indicated that substantial amounts of aliphatic ester carbonyl groups were present, verifying that the desired incorporation of CO₂ to form the polycarbonate ester had occurred.

A comparison of the reaction conditions was also performed for the reaction in aqueous formaldehyde using the basic catalyst, DMAP. This reaction matrix varied temperature (120° to 200°C) and the reaction time (12 versus 24 hr). Relevant data are given in Table 2. For the 12-hr series of runs, polycarbonate yields increased with temperature as follows: 120°C, 4%; 150°C, 5%; 175°C, 9%; 200°C, 11%. Increasing the reaction time to 24 hours at 150°C increased the yield from 5% to 7%. The molecular weight of the polymer products was about 20,000 daltons for most of the reactions, but was 40,000 for the reaction at 175°C.

Two disadvantages of the aqueous formaldehyde became obvious during these initial studies: 1) the product polymers are not easily separated from the reactant formaldehyde and oligomers, owing to similarity in solubility and difficulty in distilling the formaldehyde off without decomposition; 2) the aqueous formaldehyde contains methanol (normally 5%–15% present in commercial formalin solution) that could cap the ends of the chains as an acetal linkage. Methanol and formic acid are also formed as byproducts in the reaction via the Cannizzaro reaction of aldehydes in base. Although it is displaceable from the end formaldehyde unit, it would inhibit the reaction and prevent the reaction with the CO₂.

TABLE 2

| Reactions of Aqueous Formaldehyde | | | | | | | |
|---|---------------|---------|----------|----------|---------------------------|------------|------------------------------|
| Aldehyde | Catalyst | Solvent | Temp, °C | Time, hr | Polymer | Solubility | M _w (yield) |
| Formaldehyde (40 mL, 37%) + Ammonium Carbonate (42 g) | DMAP (2.37 g) | Water | 120 | 24 | Orange solution (1.21 g)* | Water | 20,000 (58%) 19,500 (42%) |
| Formaldehyde (40 mL, 37%) + Dry Ice (16 g) | DMAP (2.37 g) | Water | 120 | 24 | Orange solution (1.21 g)* | Water | 20,000 (58%) 19,500 (42%) |
| Formaldehyde (40 mL, 37%) + Dry Ice (16 g) | DMAP (2.37 g) | Water | 150 | 12 | Orange solution (1.63 g)* | Water | 85,000 (2%) 20,000 (98%) |
| Formaldehyde (40 mL, 37%) + Dry Ice (16 g) | DMAP (2.37 g) | Water | 150 | 24 | Orange solution (2.24 g)* | Water | 16,000 (51%) 15,500 (49%) |
| Formaldehyde (40 mL, 37%) + Dry Ice (16 g) | DMAP (2.37 g) | Water | 175 | 12 | Orange solution (2.84 g)* | Water | 40,000 (100%) |
| Formaldehyde (40 mL, 37%) + Dry Ice (16 g) | DMAP (2.37 g) | Water | 200 | 12 | Orange solution (3.1 g)* | Water | 21,000 (48%) 20,000 (52%) |

* Yield based on GPC data.

Paraformaldehyde Reactions

An investigation of the reactions of paraformaldehyde with CO₂ was conducted in ether and ester solvents at 120°C (see Table 3). The products were compared for reactions with two basic catalysts, DMAP and DABCO, in two solvents, MTBE and dioxane. The molecular weights of the products were determined by high-pressure GPC. In MTBE solvent, the stronger of the base catalysts, DMAP, resulted in the highest yields of polycarbonate, but the molecular weight of the product (12,000) was lower than that obtained with DABCO (19,000 and 23,000, two peaks). Yields in dioxane were similar for the two bases. Reactions in the ester solvent (ethyl acetate) gave no polymer product. The reaction products had limited solubility in dioxane, so were easily separated as a viscous liquid by decantation of the solvent. This product exhibited high water and ethanol solubility. IR spectroscopy confirmed its polycarbonate structure.

TABLE 3

| Reactions of Paraformaldehyde | | | | | | | |
|--|----------------|-----------------|-----------|----------|-----------------------|------------|--|
| Aldehyde | Catalyst | Solvent | Temp., °C | Time, hr | Polymer | Solubility | M _w (yield) |
| Paraformaldehyde (15 g) + Dry Ice (16 g) | DMAP (2.37 g) | Dioxane (40 mL) | 120 | 48 | Viscous oil (6.5 g) | Water | 85,000 (16%) 23,000 (48%) 22,000 (37%) |
| Paraformaldehyde (15 g) + Dry Ice (16 g) | DMAP (2.37 g) | Dioxane (40 mL) | 120 | 24 | — | — | — |
| Paraformaldehyde (15 g) + Dry Ice (16 g) | DABCO (3.58 g) | Dioxane (40 mL) | 120 | 24 | Viscous oil (3.5 g) | Water | — |
| Paraformaldehyde (15 g) + Dry Ice (16 g) | DMAP (2.3 g) | Dioxane (30 mL) | 175 | 12 | Viscous oil (10.33 g) | Water | 23,000 (100%) |
| Paraformaldehyde (22 g) + Dry Ice (24 g) | None | Dioxane (40 mL) | 120 | 24 | — | — | — |
| Paraformaldehyde (15 g) + Ethanolamine (30.5 g) + Dry Ice (16 g) | DABCO (2.3 g) | Dioxane (40 mL) | 120 | 24 | Viscous oil (51 g) | Water | <1000 (86%) 19,000 (12%) 45,000 (1%) |

Higher-temperature reactions of paraformaldehyde were also investigated. Reactions of paraformaldehyde with CO₂ in dioxane solvent (DMAP catalyst) at 175°C for 12 hr gave a 33% yield compared with a yield of 21% for the reaction at 120°C for 48 hr. The molecular weights were

similar for the two reactions (23,000). Thus temperature has a very significant effect in increasing the reaction yields, but does not significantly affect the molecular weights.

Paraformaldehyde gave higher yields of polymer than aqueous formaldehyde. The reaction of paraformaldehyde required the catalyzed depolymerization to the reactive monomer *in situ*. When paraformaldehyde was heated in dioxane at 120°C for 24 hr, no formaldehyde was formed. However, when paraformaldehyde was heated in dioxane in the presence of 4-dimethylaminopyridine, a significant amount of formaldehyde was formed. Quantitative analysis was not performed. Trioxane does not decompose to formaldehyde in base and therefore did not react to form polymer.

Reactions of Trioxane

Trioxane, the trimer of formaldehyde, is easily formed from formaldehyde and represents a soluble form. One reaction of trioxane was attempted with CO₂ with the DMAP catalyst at 150°C. No polymer formed in the reaction. The basic catalyst was not effective in breaking down the trioxane to formaldehyde for the copolymerization.

Reactions with Glycol Comonomer

Incorporation of ethylene glycol as a comonomer was attempted to determine if additional stability would result from the presence of the glycol or 1,2-dioxy unit in the chain. This unit would be expected to be more stable than the vicinal acetal or 1,1-dioxy unit that results from polymerization of the aldehydes. Thus, the polymerization of CO₂ with paraformaldehyde and 25% ethylene glycol in a dioxane solvent and DABCO catalyst was carried out. The ethylene glycol unit was also expected to modify the crystallinity of the chains by acting as a "spacer" group.

The copolymer products obtained with ethylene glycol contained 58% of a significantly higher-molecular-weight polymer (42,500 daltons) in addition to the normal 20,000-dalton polymer. The products were still soluble in water. Further reactions with epoxide and other comonomer mixtures are needed to understand and optimize the copolymerization reaction chemistry.

Copolymerization of Other Aldehydes

The scope of the acetal copolycarbonate reaction was expanded to include other aldehydes. Reactions of acetaldehyde were conducted with carbon dioxide in dioxane (DMAP catalyst) at 150°C (see Table 4). A low yield of polymer was obtained. The condensation product, crotonaldehyde, and low-molecular-weight oligomers were present. A repetition at this temperature gave similar results. A reaction temperature of 175°C gave higher yields than the reactions at 150°C. In contrast to the formaldehyde copolycarbonates, the polymer products from the acetaldehyde polymerization were not water-soluble. The acetaldehyde copolycarbonate is in fact soluble in dioxane and THF. The molecular weight of the product from the higher-temperature reaction (19,000) was similar to that from the 150°C reaction. With the basic catalyst, the major products result from condensation rather than copolymerization. Reactions of a second aldehyde (furfuraldehyde) with CO₂ were also investigated at 120°C. The product was, however, only partially soluble and appeared to have been converted to a pitch under the reaction conditions.

TABLE 4

| Reactions of Acetaldehyde | | | | | | | |
|--------------------------------------|---------------|-----------------|-----------|----------|-----------|------------|------------------------------|
| Aldehyde | Catalyst | Solvent | Temp., °C | Time, hr | Polymer | Solubility | M _w (yield) |
| Acetaldehyde (22 g) + Dry Ice (16 g) | DMAP (2.37 g) | Dioxane (40 mL) | 150 | 12 | (0.73 g)* | Dioxane | 86,000 (35%) 20,000 (97%) |
| Acetaldehyde (22) + Dry Ice (16 g) | DMAP (2.3 g) | Dioxane (40 mL) | 175 | 12 | (5.73 g)* | Dioxane | 19,000 (100%) |

* Yield based on GPC data.

Lewis Acid Catalysis

A large number of Lewis acid catalysts have been tested in other laboratories for the related copolymerization of epoxides with CO₂ (2-7). One of these catalysts, zinc bisanil (7), was prepared for the reactions of CO₂ with paraformaldehyde and acetaldehyde. The function of the acid catalyst is to break down the paraformaldehyde or trioxane, as well as catalyze the copolymerization.

Several forms of the Zn bisanil catalyst were investigated. The methoxide form gave a white polymeric film on top of an orange solution. The polymeric film was separated by filtration. The white film was air-dried and weighed. The orange solution was evaporated to remove solvent. Upon removal of solvent, a highly viscous orange oil was formed. The oil was completely soluble in water and was analyzed by GPC. Relevant data are given in Table 5.

TABLE 5

Zinc Bisanil Complex-Catalyzed Reactions of Paraformaldehyde and CO₂

| Aldehyde | Catalyst | Solvent | Temp., °C | Time, hr | Polymer | Solubility | M _w (yield) |
|----------------------------|--|--------------------|-----------|----------|---------------------------------------|------------|---|
| Paraformaldehyde (15 g) | Bisanil + NaOMe +ZnCl ₂ (1.08 g) | Dioxane (40 mL) | 150 | 20 | Orange oil (8.71 g) White solid | Water | 21,500 (18%) 18,000 (6%) 1000 (52%) <1000 (rest) |
| Paraformaldehyde (15 g) | Bisanil ZnCl ₂ (3.54 g) | Dioxane (40 mL) | 150 | 12 | Orange oil (4.62 g) | Water | |
| Paraformaldehyde (15 g) | Bisanil ZnTCA (0.5 g) | Dioxane (40 mL) | 150 | 12 | Orange oil (6.26 g) | Water | 85,000 (1.5%) 24,000 (3%) 21,000 (36%) 17,000 (24%) 13,000 (7%) |

The methoxide form of the catalyst gave the most product, but only a portion of it was the 21,000-dalton polymer. Most was the oligomers. The chloride form gave the least product, and since it was not soluble in water, it has not yet been analyzed in the GPC system. The trichloroacetate form was reasonably successful in producing the 17,000- to 21,000-dalton product.

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